



## Topical Perspectives

# Intra-molecular electron communication, spectroscopic and conformational stability of the newly developed urethane modified polyetheramide coatings: Computational methods



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## ABSTRACT

There have been constant research efforts towards the development of new and thermally stable resins, containing properties to outdoor usage, such as high quality of adhesion, as well as resistance to water and acid, amongst others. In this computational study, the spectroscopic properties were calculated, also the intramolecular electronic communication, susceptibility, as well as conformational changes in two monomers of potential resins, namely Albiziabenth oil polyetheramide (ABOPeTA) and urethanated Albiziabenth oil polyetheramide (UABOPeTA), as well as their precursor, namely hydroxyethyl albiziabenth oil amide (HEABOA). Many of these computed properties clearly show that the urethane linkage group in UABOPeTA acts as a strong electron withdrawing group, consequently causing the rest of the molecule to be more nucleophilic. This leads to an increase in the stability of UABOPeTA, as compared the rest of the molecules, as evidenced by an increase in the intramolecular energy of interaction, as well as negative values of the polarizability exaltation index ( $\Gamma$ ). Further UABOPeTA is also associated with higher non-linear optical properties, in terms of the hyperpolarizabilities ( $\beta$ ) and increased aromaticity, than for molecules ABOPeTA and HEABOA. The conformational folding of molecule UABOPeTA is characterized by larger values of the bisphenol-A linkage bond angle C...C...C, contrary to the angle observed in molecule ABOPeTA. This is a direct effect of hiding the urethane unit in the cleft of the folded UABOPeTA, which clearly leads to an increase in the hydrophobicity of UABOPeTA.

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## 1. Introduction

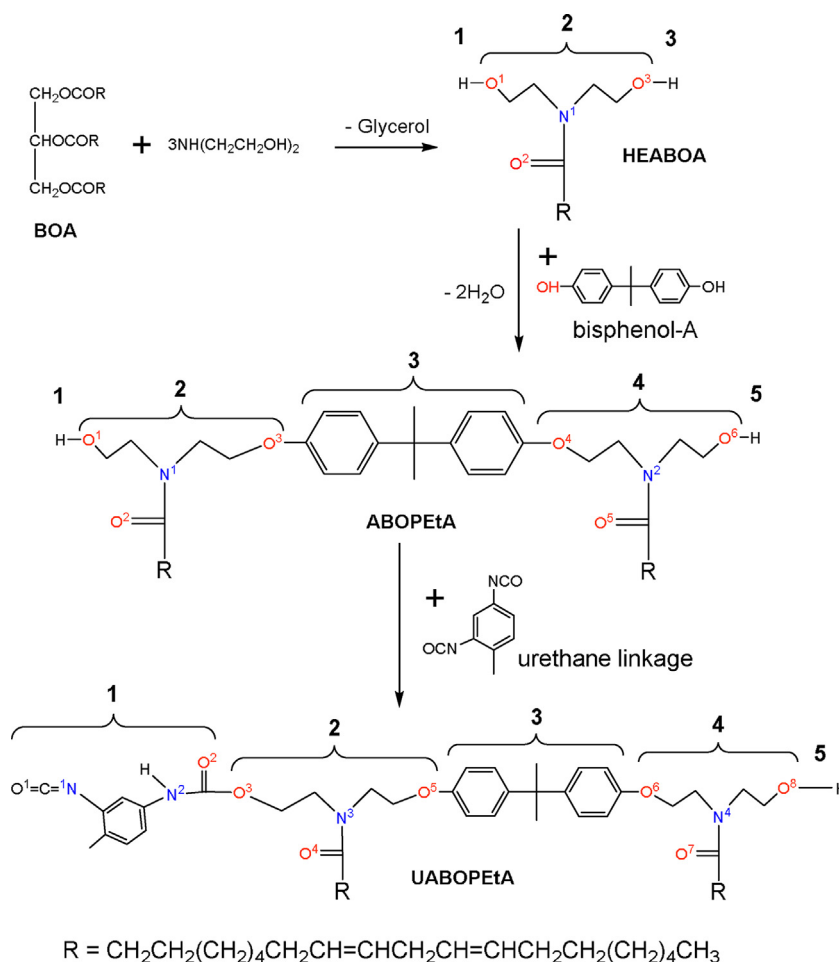
In an attempt to derive environmentally friendly resins with good adhesion properties, the synthesis of the polyetheramide resin, called Albiziabenth oil polyetheramide (ABOPeTA), has been reported in literature [1]. The molecule ABOPeTA was derived from the condensation polymerization reaction of bisphenol-A (2,2-Bis(4-hydroxyphenyl)propane) with the *N-N*-bis (2-hydroxyethyl) fatty amide of Albiziabenth oil, called hydroxyethyl albiziabenth oil amide (HEABOA)[1], as shown in Fig. 1. The molecule HEABOA itself was synthesized by the condensation reaction of diethanolamine with Albiziabenth oil (BOA). Further modification of the resin ABOPeTA, with the isocyanate moiety of toluene, namely 2,4 di-isocyanate (referred to as a urethane linkage), resulted

in an additional compound, called urethanated Albiziabenth oil polyetheramide (UABOPeTA). The significance of this modification was reported to be an effort to produce a resin compound which is environmentally friendly, with good adhesion, improved thermal stability, abrasion resistance, toughness, as well as water and acid resistance, which is also good for outdoor usage [1]. The schematic representation for the syntheses of these three compounds is shown in Fig. 1.

The aim of this computational study is to examine both the atomic and molecular changes in compounds HEABOA (HE), ABOPeTA (AB) and UABOPeTA (UA), which resulted in the improved resin properties that have been observed experimentally for UA. Therefore, the spectroscopic and electronic properties, as well as the conformational folding of the molecules in aqueous medium, are presented in this paper, in order to provide some insight into the improved qualities of UABOPeTA, which were observed experimentally.

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**Fig. 1.** The schematic representation of the synthesis of molecules HEABOA, ABOPEtA and UABOPEtA from Albiziabenth oil (BOA), as reported in literature [1], also indicating the fragmentation used in the computation.

## 2. Computational methods

### 2.1. Quantum chemistry calculations

The Gaussian 09 (G09) program [2] was used to optimize the three molecules HE, AB and UA, as well as compute their quantum properties. The modified hybrid DFT functional Perdew-Wang exchange by Adamo and Barone, combined with PW91 correlation (mPW1PW91) [3] and basis set 6-311G(d,p), was used for the optimization in the gas phase. The B3LYP and UB3LYP functional were used to compute the excitation and the hyperfine properties respectively. Other computed properties are the dipole moment ( $\mu_i$ ), linear polarizability tensors ( $\alpha_{ij}$ ) and first hyperpolarizability tensors ( $\beta_{ijk}$ ) of these molecules, which were derived from the energy expression of a molecule under a static electric field (F):

$$E = E^0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{26} \gamma_{ijkl} F_i F_j F_k F_l - \dots$$

$E^0$  is the energy in the absence of an electronic field,  $\gamma_{ijkl}$  is the second hyperpolarizability tensor and the labels  $i, j,$  and  $k$  indicate the  $x, y,$  and  $z$  components respectively [4]. The dipole was computed by formula  $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$  while the NMR and bond spin-spin coupling constants  $J(A,B)$  were computed using the GIAO method [5,6], as implemented in the G09 program.

The Natural Bond Orbital (NBO) analysis [7] and Natural Energy Decomposition Analysis (NEDA) [8] and their associated computed properties were obtained, using the NBO 6.0G program [9], as

implemented in FIREFLY 8.1.G [10], which is partially based on the GAMESS (US) [11] source code.

### 2.2. Molecular dynamic calculations

Program Amber 14 [12,13] was used for all the molecular dynamic (MD) calculations of the three molecules HE, AB and UA, in an explicit TIP3P water solvent, in an orthorhombic box of size 12 Å around the complex, with solute atoms kept within 8 Å from any side of the box [14]. The force field of each molecule was derived using the restrained electrostatic potential (RESP) method. The geometries were reoptimized again with G09, applied HF/6-31G\* level of theory, and the partial atomic charges were fitted using the R.E.D package [15]. The preparation of topological and geometrical files was done using the tleap module of Amber 15. The Partial Mesh Ewald (PME) method was used for the long range electrostatic potentials calculation, setting the Van der Waals cut-off at 12 Å. The systems were firstly minimized by initial 500 steps (2.5 ps) of steepest descent, followed by 1000 steps (5 ps). Thereafter, the systems were gradually heated to 300 K, in canonical ensemble MD simulation for 25 ps, using a Langevin thermostat with a collision frequency of  $1.0 \text{ ps}^{-1}$  and a harmonic restraint of 5 kcal/mol Å. Other steps taken were 25 ps of constant pressure and temperature (NPT) simulation to control the density of the systems, 250 ps of equilibration at a temperature of 300 K and 1 bar pressure, which was followed by 10 ns of normal MD. All the bond lengths involving hydrogen atoms were restrained by the SHAKE algorithm [16]. The all-atom enhanced sampling method of Accelerated Molecular

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